Study of photoresist etching and roughness formation in electron-beam generated plasmas

Bryan J. Orf
Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742 and Institute for Research in Electronics and Applied Physics, University of Maryland, College Park, Maryland 20742

Scott G. Walton and Darrin Leonhardt[a)]
Plasma Physics Division, U.S. Naval Research Laboratory, Washington, DC 20375-5346

Gottlieb S. Oehrlein
Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742 and Institute for Research in Electronics and Applied Physics, University of Maryland, College Park, Maryland 20742

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A modulated, electron-beam generated plasma processing system was used to study plasma-polymer interactions for 193 and 248 nm photoresists (PRs) that differed significantly in polymer structure. Because of the low plasma potential of the electron-beam generated plasma, the authors were able to study plasma etching and surface roughening of the photoresists at very low ion energies (<5 eV) without sacrificing high ion flux ($>10^{14}$ cm^{-2}). Typical conditions in the experiments were 2 kV/4 ms electron-beam pulses with a 20 ms period. The effects of ion bombardment energy, chemically assisted etching using fluorine, and the presence of a thin fluorocarbon overlayer on surface roughness formation during PR etching were examined. Gas mixtures containing SF_6 resulted in much higher etch rates and an increased surface roughness relative to values measured in pure Ar plasmas. However, the rms roughness per nanometer of photoresist removed was greater for pure Ar plasmas. Overall the 248 nm PR showed less surface roughness than 193 nm PR after identical treatments, which was explained by a higher etching rate of the 193 nm photoresist material. Finally, it was found in a pure argon plasma that the thickness of a fluorocarbon overlayer determined the roughness of the underlying photoresist; specifically, thicker layers resulted in smoother PR surfaces after plasma exposure.
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I. INTRODUCTION

Plasma modification of polymer surfaces has been widely applied in materials research.[1–5] Plasmas can be used to tailor surface energy and reactivity of polymeric materials without interfering with the bulk polymer properties. Input power, pressure, degree of ionization, and other plasma parameters all affect the outcome of plasma-polymer interactions.[6–9] The continual development of state-of-the-art photoresists used in the semiconductor industry requires particular diligence to understand plasma-polymer interactions due to the various chemical structures and reduction of material thicknesses. The methacrylate main chain used in 193 nm photoresist (PR) has been found to be less robust than the aromatic polymer-based 248 nm PR when exposed to standard argon and C_4F_8 based discharges,[10,11] as well as having an increased surface roughness.[12] The Naval Research Laboratory has developed a plasma processing tool called the large area plasma processing system (LAPPS) that utilizes a high energy (>1 keV) electron beam (e-beam) for plasma generation, which provides high density plasmas with very low electron temperatures.[13–18] We have applied the high degree of process control afforded by LAPPS in an effort to shed light on the surface roughening problem seen in the processing of photoresist materials and performed comparative etching studies at low ion energies using a 193 and 248 nm PRs. These studies of plasma-polymer interactions were performed using plasmas produced in SF_6/Ar mixtures and focused on how the ion bombardment energy, neutral fluorine reactivity, and a fluorocarbon (FC) overlayer affect plasma-photoresist interactions.

II. EXPERIMENTAL SETUP AND PROCEDURES

A. Photoresists

The first material was a standard 248 nm PR consisting of a stable aromatic ring structure. The second was a 193 nm PR, which is a methacrylate main chain containing highly reactive lactone and adamantane-based functional groups (Fig. 1). This 193 nm PR was chosen for its critical role in the development of nanometer scale feature evolution in the semiconductor industry. Both photoresist films were obtained from Rohm and Hass and spin coated to a thickness of about 410 nm on silicon substrates.

[a)]Present address: Fusion UV Systems, Inc., Gaithersburg, MD 20878. Electronic mail: dleonhardt@fusionuv.com

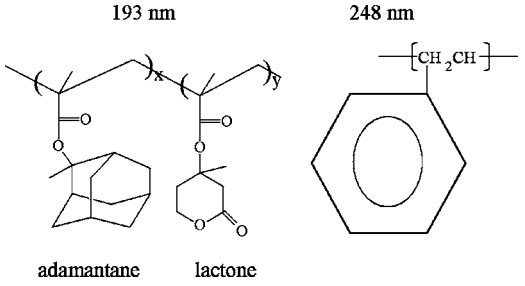

FIG. 1. Chemical Structures of 193 and 248 nm photoresist polymers.

B. LAPPS

A schematic diagram of the LAPPS is shown in Fig. 2. The design and operation of LAPPS have been discussed previously theoretically[13,14] and experimentally.[15–18] Briefly, a linear hollow cathode was used to generate a beam of high energy electrons which in turn generates a plasma over the beam volume. The hollow cathode was driven by a 2 kV, 4 ms pulse operating at a variable duty cycle (1%–50%). The generated e-beam passed through a slot in a grounded anode and terminated at a second grounded anode at the end of the chamber. A 165 G magnetic field was applied by Helmholtz coils to collimate the electron beam. A processing stage was located parallel to the beam axis. The stage face was located 2 cm from the axis. On the isolated stage electrode, a thin 5 cm diameter anodized aluminum plate was attached to the stage via screws. The substrates were cut into 1×3 cm^2 samples and were adhered to the anodized sample holder via silver print epoxy. The chamber had a base pressure below 8×10^{-7} Torr provided by a turbomolecular pump. The system's operating pressure was maintained at a constant total flow by a manual throttle valve at the entrance to the pump.

A rf signal was synchronized with the e-beam pulse and applied to the stage to provide a dc self-bias voltage up to 50 V. The measurements of the rf voltage and currents to the stage were done in air at the electrical feedthrough with a $10\times$ oscilloscope probe and current transformer (Pearson Electronics Model 2877). Etching times corresponded to the pulse period ($T_{on}+T_{off}$) multiplied by the number of pulses. The stage temperature was kept at (22±4) °C with a recirculating water bath during all experiments.

"Standard conditions" used during the processes were $T_{on}=4$ ms and $T_{off}=16$ ms with a total run time of 12.5 min, and a total gas flow rate of 50 sccm (sccm denotes cubic centimeter per minute at STP). Typical operating pressure was about 25 mTorr in the pure Ar experiments, and 95 mTorr for SF_6/Ar experiments. These pressure differences permitted similar ion currents when a −10 V dc was applied to the conductive stage front.

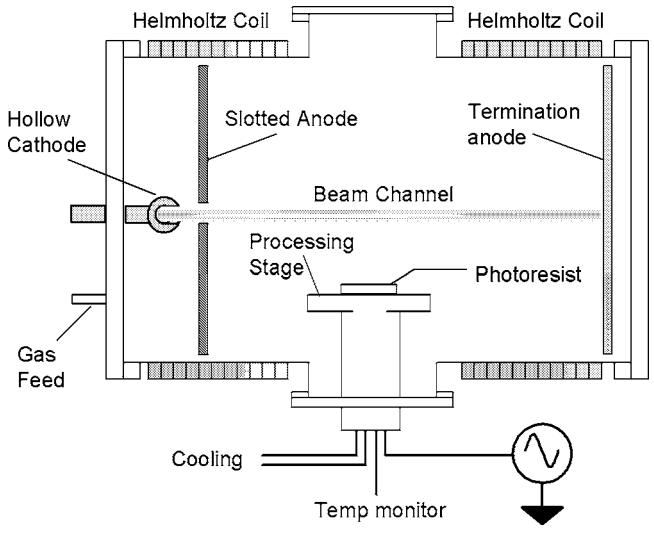

FIG. 2. Schematic diagram of LAPPS etching chamber.

C. *Ex situ* analysis

Film thicknesses were determined using an automatic ellipsometer with a 632.8 nm He–Ne laser.[19,20] Although the index of refraction of the surface (2–3 nm) had been modified, this change poses a very small effect on the accuracy of the thickness measurement. Furthermore, once a steady state was reached (assumed for all samples), the slight variation in n remains constant. The change in film thickness was used to determine etch depth (ED), and thus the etching rates, which was simply the ED divided by the total run time (ER =ED/run time). Surface roughness was measured by a Digital Instruments BioScope atomic force microscope (AFM). All of the AFM scans on the samples were done over an area of 1 μm^2 at a scan rate of 1 Hz.

D. Thin flourocarbon (FC) layer

The thin FC layer was added to the samples using a capacitively coupled plasma system described elsewhere.[21] The properties of these deposited FC films have been described by Zheng *et al.*[22] and also by Ling *et al.*[10,23] Briefly, the deposition used remote 10% C_4F_8 in Ar or pure C_4F_8 plasmas with a roof structure over the samples[24] and deposition times of 1, 2, 5, and 10 min. The depositions were run at 30 mTorr with a 40 sccm total gas flow rate, and the stage was unbiased. "Thin" FC films (0–1.5 nm) were deposited using the 10% C_4F_8 plasma and "thick" films (up to 4 nm) were grown in the pure C_4F_8 plasma, as measured by ellipsometry.

III. RESULTS

The surface roughness and etch rates of the PRs as a function of the rf induced dc self-bias voltage are shown in Fig. 3 for both etching plasma gas compositions at standard conditions. In all of the data presented, the relative error was about 10%, based on experiments repeated over the period of more than a year, with multiple measurements on specific samples. To maintain the same ion currents to the stage, the pressure for the Ar plasma was increased slightly with the rf bias (24–25 to 27.5 mTorr) while the 5% SF_6 mixture was held constant at 95 mTorr. The photoresists showed similar trends when exposed to each plasma, although the 193 nm PR had a greater roughness and etch depth than the 248 nm

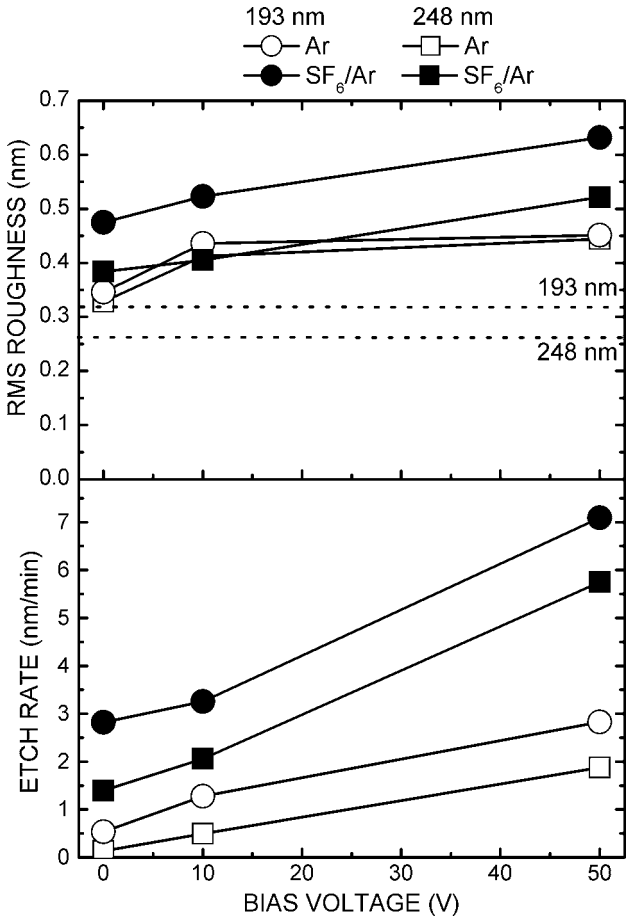

FIG. 3. Etch rate and rms roughness values of PRs as a function of rf induced dc self-bias in Ar and 5% SF_6/Ar electron-beam generated plasmas. Initial photoresist rms roughness values are shown by dotted lines.

material. Figure 3 shows that the photoresist etch rates monotonically increased with the rf bias voltage in all cases. When SF_6 was added to the plasma gas (solid symbols), the measured surface roughness increased with bias voltage, whereas the surface roughness seemed to saturate for the pure Ar experiments (open symbols). The rms roughness per nanometer of PR etched at these bias voltages is shown in Fig. 4. The amount of rms roughness was reduced when SF_6 was added to the plasma gas, and that effect became more pronounced as the bias decreased. Even though the overall surface roughness was found to be greater for the 193 nm PR (see Fig. 3), the relative roughness shown in Fig. 4 was found to be less for the 193 nm material.

Figure 5 shows the etching behavior as the percentage of SF_6 was increased in the gas mixture. Here, standard conditions and a fixed 10 V self-bias were used. Both the etch rate and surface roughness increased with increasing fluorine content and appeared to saturate above 10% SF_6. Here again, the 193 nm PR had a greater etch rate and rms roughness compared to the 248 nm PR.

Shown in Fig. 6 is the effect of modulated plasma production on the etching behavior, by varying T_{off} with a fixed T_{on} duration (4 ms) in a 5% SF_6/Ar plasma. The stage self-bias was 10 V. The total run times were varied to provide an

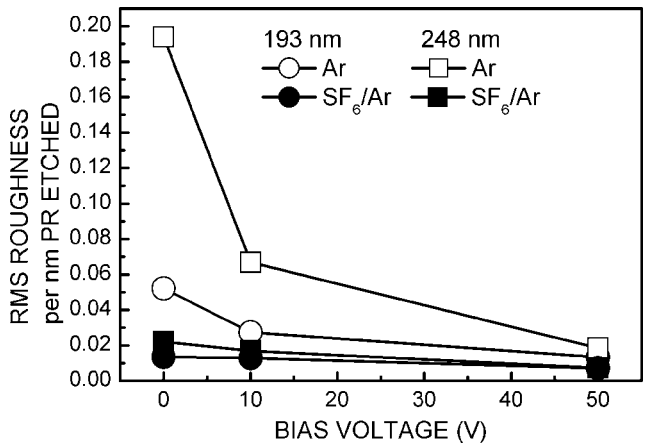

FIG. 4. rms roughness per nanometer PR etched vs bias voltage. The samples were run at standard conditions discussed in text.

equal number of plasma pulses, thus Fig. 6 shows the etch depth per pulse and the surface roughness change as a function of T_{off}. Both PRs showed an increased etch depth and surface roughness for increased afterglow (T_{off}) times.

The effect of a thin fluorocarbon (FC) layer on the PR surface evolution in pure Ar plasmas was investigated and shown in Fig. 7 are AFM images of 193 nm PR obtained before and after LAPPS exposure, for both thin and thick FC layers. For all of the FC samples a 50 V bias was used during etching and plasma exposure times were held constant.

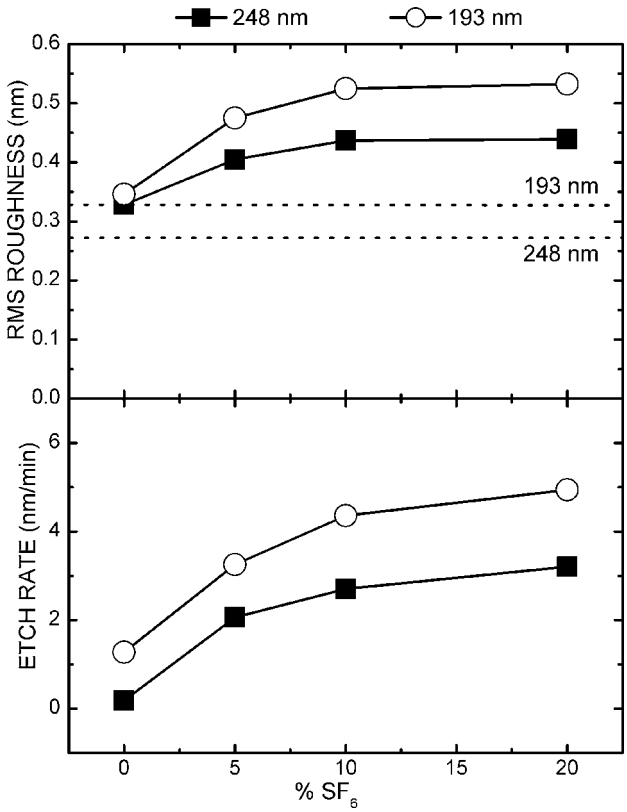

FIG. 5. Etch rates and rms roughness of PRs at various percentages of SF_6 in plasma gas mixture. A 10 V bias was used.

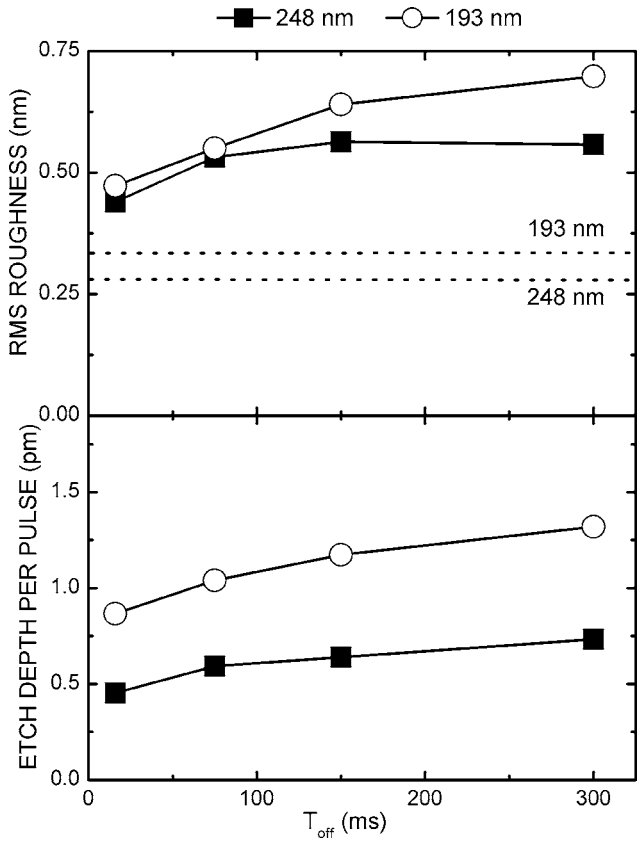

FIG. 6. Etch depth per pulse and rms roughness of PRs at varying T_{off} times for T_{on}=4 ms in 5% SF_6/Ar plasmas. Experiments were performed at otherwise standard conditions with a 10 V bias.

The final PR surface roughness was reduced relative to the initial FC layer roughness, but the overall roughness values were larger than seen for PR without a FC layer. Figure 8 quantifies the effect of thick FC films (pure C_4F_8 deposited) on the PR etch depth and rms roughness post-LAPPS exposure. The etch depth was the net etching depth of the sample without considering the removal of the FC film. For both PRs the etch depth was strongly dependent on the FC film

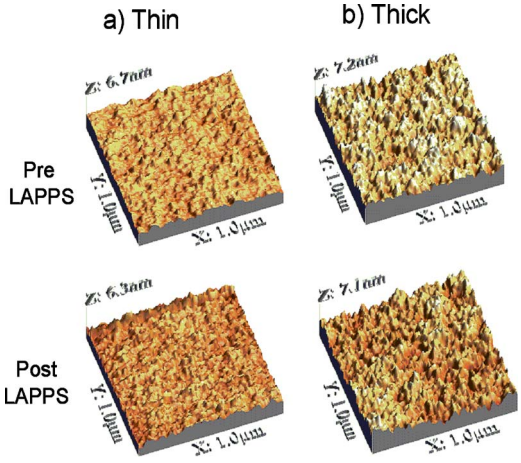

FIG. 7. AFM images of FC films deposited on 193 nm photoresist before and after Ar etching with a 50 V bias. (a) Thin and (b) thick FC layers.

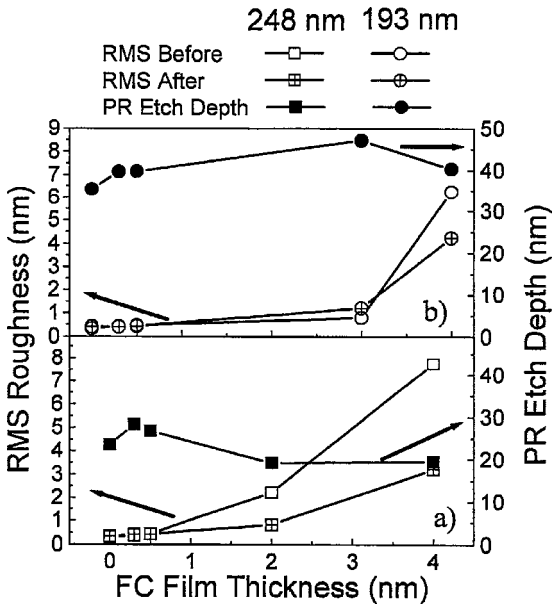

FIG. 8. (a) 248 nm PR rms roughness and PR etch depth of FC layer/PR stack in an Ar plasma as a function of the FC film thickness for thick FC films. (b) Same data for 193 nm PR. The FC film was deposited in a pure C_4F_8 plasma and the etching experiments were done in a pure Ar plasma and 50 V substrate bias.

thickness. There was an increase in the surface roughness with thickness for the as-deposited FC films, which decreased upon etching through to the bulk PR. Figure 9 shows the change in PR etch depth and rms roughness for thin FC films (10% C_4F_8 in Ar deposited) after an Ar plasma exposure with at 50 V self-bias. An increase in the surface roughness was seen with the FC film thickness; however, little change was observed before and after LAPPS exposure. Although the observed changes were small in Figs. 8 and 9, they were consistently greater than the data spread experienced throughout these tests.

IV. DISCUSSION

The low plasma potential of LAPPS enabled the study of PR etching and surface roughness evolution down to very low ion energies. Our results indicate that there was finite photoresist etching in pure Ar without a rf bias and that the etch rate of 193 nm PR was higher than that of 248 nm PR. Without rf induced self-bias, the ion energy[16] was <5 eV and etching should be dominated by the neutralization of the Ar^+ ion (15.7 eV ionization potential) and possible deexcitation of metastable species (11.5 eV). However, since the production of argon metastables is three orders of magnitude lower than the production of ions at 2 keV electron impact energies, the role of metastable species is considered minimal in this system.[25]

A largely physical etching mechanism of Ar plasmas and one with a chemical etching component (5% SF_6/Ar) were studied to delineate the etching behavior and surface evolution of the two PRs. Over the entire range of ion energies studied, the etch rates were significantly increased by the addition of the chemical component although the surface

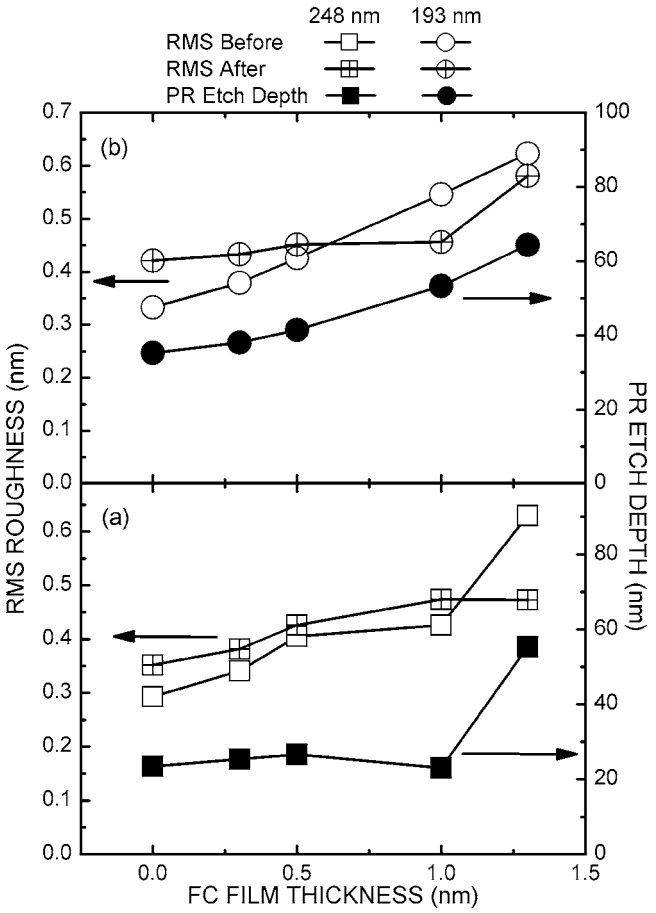

FIG. 9. (a) 248 nm PR rms roughness and PR etch depth of FC layer/PR stack in an Ar plasma as a function of the FC film thickness for thin FC films. (b) Same data for 193 nm PR. The FC film was deposited in a 10% C_4F_8 in Ar plasma and the etching experiments were done in a pure Ar plasma and 50 V substrate bias.

roughness change was not as appreciable. Chemically enhanced etching also took place at a higher rate for the 193 nm PR than for the 248 nm PR. Interestingly, when the rms roughness was normalized to the etch depth, the 248 nm PR roughness was greater than the 193 nm PR (Fig. 4). Moreover, the roughness per nanometer of etch depth was much greater for a pure Ar plasma than for a SF_6/Ar plasma (Fig. 4), which seemed to indicate that the fluorine attack contributed more to etching than to roughening the PR surfaces.

The pulsed nature of LAPPS was used to further examine the chemical aspect of the etching characteristics. Both etch depth per pulse and rms roughness of the 193 nm PR was greater than the 248 nm PR, which was consistent with the notion that the 193 nm PR is more reactive than the 248 nm PR. By increasing the afterglow duration (T_{off}), we found that the rms roughness as well as the etch depth increased for the same total T_{on} exposure. Although the afterglow period must be dominated by the attack of long-lived neutral species, surface modification continued to progress in the absence of ion-driven mechanisms. It cannot be entirely clear whether material removal occurred during the afterglow phase, or whether the desorption of loosely bonded reaction by-products must be stimulated by ion bombardment, which was only available during the plasma phase. However, if enhanced surface attack in the afterglow occurs, it should be more pronounced for a reactive surface and thus could explain the difference in rms roughness between the two materials. The continued increase in the rms roughness of the 193 nm PR with the longer afterglow exposure compared with the apparent saturation in roughness for 248 nm PR is consistent with a continual chemical attack of the more reactive (193 nm PR) material during the afterglow period. The less reactive 248 nm PR had an apparent limit to roughening in the absence of ion bombardment.

It is well known that selective SiO_2 etching is possible through FC polymer deposition and is strongly dependent on the ratio of fluorocarbon radicals to atomic fluorine.[26–30] Thin FC films typically deposited in FC etching plasmas were found to increase the etch rate of the PRs in the absence of etch gas; however, no significant change in the rms roughness was introduced between a PR with a small (<1 nm) FC layer and one without. Very large FC depositions (4 nm) resulted in large initial rms roughness values; however, after etching with LAPPS, the surface roughness was found to be smoother than that of the initial FC layer. Therefore, although the FC film surface roughness can be transferred to photoresist underlayers, we observed that as the FC thickness increased, etching produced a rms roughness lower than the original FC film (Fig. 8). Very thin FC layers (<1 nm) showed a less pronounced effect on the final PR roughness (Fig. 9). This may be due to the larger amount of fluorine available from thicker FC films. As observed in Fig. 5, even slight increases in plasma fluorine content can rapidly increase both the roughness and etch rate of these PR materials.

V. CONCLUSIONS

An e-beam produced plasma was used to investigate the response of PR material to low energy ions and chemically reactive species. In these experiments we have examined the effects of ion bombardment energy, fluorine addition to Ar plasmas, and the presence of a thin FC layer on the etching rates and surface roughness of 193 and 248 nm photoresist materials. Low energy (<5 eV) ion bombardment caused an appreciable and reproducible increase in the roughness of the photoresist surfaces, which increased further when small amounts of fluorine were added to the plasma gas mixture. However, the amount of surface roughness per nanometer of PR etch depth in a fluorinated plasma decreased relative to a pure Ar plasma. Further, it was shown that the roughness of a deposited FC layer $\geqslant 1$ nm in thickness, as found in semiconductor etch processes, can impact the surface roughness of the etched PR underlayers. However, this effect was dependent upon both the initial FC layer thickness and roughness.

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